# Lecture 12: Phonon heat capacity

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- **Phonon heat capacity**
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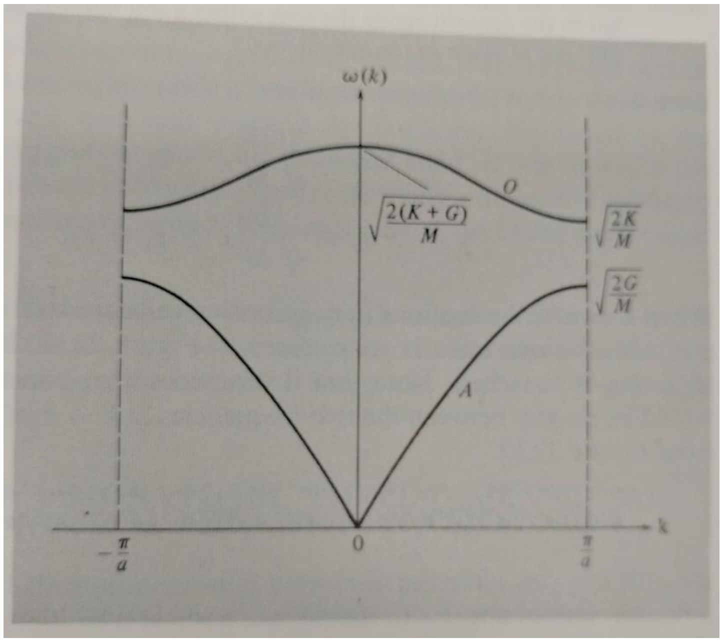
## Review

By considering discrete masses on springs in a crystalline solid, we have derived wave dispersion $(\omega\ vs\ K)$ relations. There are two general types of phonons: acoustic and optical. The former have zero frequency at k=0 and are associated with propagation of sound waves in a solid, and the latter have non-zero frequency at k=0 and can couple to light.



In 3 dimensions, each branch has one longitudinal mode (displacements parallel to wave propagation) and two transverse modes (displacement perpendicular to wave propagation). Optical modes can only occur if there is more than one atom per basis.

We have spent the previous three lectures building up the formalism of waves in solids. It turns out that just like light waves sometimes behave like particles instead, elastic waves in solids also have a wave/particle duality.

A quantum of crystal lattice vibration is called a **phonon.** Generally, the suffix –on in physics connotes something that behaves as a discrete particle. Crystalline solids support many different types of 'quasiparticles'—particle-like excitations which are the result of many-body interactions in a crystal and do not exist outside a crystalline solid.

Going back to the definition of a quantum harmonic oscillator, the energy of an elastic mode of angular frequency $\omega$ is:

$$E = \left(n + \frac{1}{2}\right)\hbar\omega$$

$\frac{1}{2}\hbar\omega$ is the zero point energy of the mode, and when $n > 0$ it means that the mode is occupied by n phonons. Phonons are bosonic particles so each mode (defined by its angular frequency $\omega$) can be occupied by more than one particle.

The particle nature of lattice vibrations in solids will become more evident in this chapter when we use it to explain various thermal properties of materials.

Also, because of boundary conditions, the wavevector or momentum, k, is also quantized. For a 1D chain, we assume that there are N atoms and periodic boundary conditions such that the 0-th atom is mapped onto the N-th atom.

Plugging this into the wave-like solution, we get:

$$e^{i(kNa-\omega t)} = e^{i(0-\omega t)}$$

$$e^{ikNa} = 1$$

$$kNa = 2\pi n \text{ (where n is an integer)}$$

$$k = \frac{2\pi n}{aN}$$

Thus, k is not a continuous variable, but it only takes on quantized solutions. However, for large N, the spacing between adjacent values is very small. Note that since the maximum **unique** values that k can take on are $\pm\frac{\pi}{a}$, there are N distinct values that k can take on. Another way to say this is that there are N 'modes' in this branch, or N available quantum states.

**Quantum harmonic oscillator: measuring occupation of normal modes**

A quantum harmonic oscillator has energy eigenvalues

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

The partition function for a discrete ensemble is defined as:

$$Z \equiv \sum_n e^{-E_n\beta}$$

It is a sum over all available states which have a characteristic energy, and each term in the sum describes the probability of a given state being occupied at a given energy based on the temperature. $\beta = 1/k_BT$ $k_B$ is the Boltzmann constant which converts temperature (in Kelvin) to units of energy (usually in Joules). The derivatives of Z are involved in all thermodynamic quantities. For a quantum harmonic oscillator, the partition function is given by:

$$Z_{QHO} = \sum_n e^{-\left(n+\frac{1}{2}\right)\hbar\omega\beta}$$

$$= e^{-\hbar\omega\beta/2} \sum_{n=0}^{\infty} e^{-n\hbar\omega\beta}$$

This is a geometric series of the form $\sum_n x^n = \frac{1}{1-x}$ if |x|<1

$$Z_{QHO} = \frac{e^{-\hbar\omega\beta/2}}{1-e^{-\hbar\omega\beta}}$$

The average energy is given by:

$$\langle E \rangle = -\frac{\partial log Z_{QHO}}{\partial\beta} = \frac{\partial}{\partial\beta}\left(\frac{\hbar\omega\beta}{2} + \log\left(1-e^{-\hbar\omega\beta}\right)\right)$$

$$\langle E \rangle = \frac{\hbar\omega}{2} - \frac{\hbar\omega e^{-\hbar\omega\beta}}{1-e^{-\hbar\omega\beta}} = \hbar\omega(\frac{1}{2} + \frac{1}{e^{\hbar\omega\beta}-1})$$

This corresponds to an average occupation value

$$\langle n \rangle_{QHO} = \frac{1}{e^{\hbar\omega\beta}-1} = \frac{1}{e^{\hbar\omega/k_BT}-1}$$

This is also known as the **planck distribution**, used to derive blackbody radiation in the context of photons. Like photons, phonons are bosons, and many can occupy a given quantum state. We will need this later. Unlike photons, there are three polarizations for each propagation direction (not two), and **k** cannot take on arbitrary values—it can only take on values in the first Brillouin zone.

### Phonon heat capacity

Heat capacity is a materials property which converts absorbed **energy** into an increase in **temperature**.

Knowing the heat capacity of a material can help you answer questions like

- If I shine a laser of known power and frequency onto a given crystalline solid (and I know the optical absorptivity of that material for that frequency of light), how much will the region exposed to the laser beam heat up?
- If I put a copper pan on a hot plate (powered by known voltage and current) what is the maximum temperature it can reach in 5 minutes?

In this derivation, we will consider the heat capacity at **constant volume**, defined as $c_V = \left(\frac{\partial U}{\partial T}\right)_V$

Where U is the internal energy and T is the temperature.

There is also heat capacity at **constant pressure** ($c_P$) which is given by the temperature derivative of the enthalpy ($H = U + PV$). The two types of heat capacity are related to each other by the thermodynamic relation $c_P - c_V = 9\alpha^2 BVT$ where $\alpha$ is the coefficient of linear thermal expansion (thermal expansion will be discussed later in chapter 5), V is the volume, and B is the bulk modulus (derived in chapter 3).

The total energy (U) of phonons at a given temperature is given by:

$$\sum_K \sum_p < n_{K,p} > \hbar\omega_{K,p}$$

Where:

- The sum over K is summing up all available momentum states (e.g. momentum is quantized, so we consider each discrete value and look at the frequency $\omega$ at that value according to the dispersion relation)
- The sum over p is summing up all 'polarizations.' This is another way of saying you are summing over all phonon branches (longitudinal acoustic, transverse acoustic, longitudinal optical and transverse optical). For a material which occupies D dimensions and has P atoms per basis, there will be a total of DP 'polarizations' with D of them being acoustic and D(P-1) of them being optical.
- Each permissible $\omega_{K,p}$ is called a **normal mode**
- $< n_{K,p} >$ is the **number** of phonons with momentum K and polarization p which are expected to be occupied at a given temperature. This is the term which allows us to take a temperature derivative to derive heat capacity because the other terms are not temperature dependent. Some general intuition about this term:
  - At a given temperature, lower frequency modes are more likely to be occupied, unless the temperature is really high
  - Every material has a maximum phonon frequency, so at sufficiently high temperature, all modes will be equally occupied

Plug the value value of $\langle n \rangle_{QHO}$ found earlier into U:

$$U = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{e^{\hbar\omega_{K,p}/k_B T} - 1}$$

It is convenient to replace the sum over K with an integral, because adjacent values of K are so close together that it is almost a continuum.

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Where $D_p(\omega)$ is the **density of states**—the number of phonon modes between frequency $\omega$ and $\omega + d\omega$ of polarization p. Densities of states are encountered in various contexts in solid state physics, and they are used to enumerate the number of quantum states available to be occupied by various particles. The units are (number of states)/energy.

$$c_v = \frac{\partial U}{\partial T} = \sum_p \int d\omega D_p(\omega) \frac{\frac{(\hbar\omega)^2}{k_B T^2} e^{\hbar\omega/k_B T}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2}$$

Finding the specific heat amounts to first figuring out the density of states. We will consider a general formulation in 3D followed by two common approximations (of which only one will be covered in this lecture).

**Density of states in three dimensions**

Use periodic boundary conditions in all three dimensions, but consider the **length** in each direction (i.e. consider a box of dimensions LxLXL=V

$$u(na) = u(na + L)$$

$$u_0 e^{i(K_x na - \omega t)} = u_0 e^{i(K_x na + KL - \omega t)}$$

$$1 = e^{iK_x L}$$

For this equality to hold, K_x can take on: the values $0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L} \ldots \pm\frac{N\pi}{L}$

Similar for K_y and K_z

The interval between k points in each dimension is

$$\Delta K = 2\pi/L$$

Thus in three dimensions, there is **one** mode per box of volume $\Delta K_x \Delta K_y \Delta K_z = \left(\frac{2\pi}{L}\right)^3 = 8\pi^3/V$

The total number of modes with wavevector less than K is given by dividing a sphere of radius K by the volume of each 'box'

$$N = \frac{\frac{4}{3}\pi K^3}{8\pi^3/V} = K^3 V/6\pi^2$$

We want $\frac{dN}{d\omega} d\omega = D(\omega) d\omega$

Use chain rule to express this in terms of K

$$\frac{dN}{d\omega} = \frac{dN}{dK} dK/d\omega$$

$$\frac{dN}{dK} = K^2 V/2\pi^2$$

Thus, we get $D(\omega) = \frac{K^2 V}{2\pi^2}\frac{dK}{d\omega}$

This is the density of states for a particular polarization, and the total density of states is found by adding up this expression for all polarizations.

Thus, if we had a closed-form expression for $\omega(K)$, we could invert it to find $K(\omega)$ and take the derivative to find the density of states.

For a three dimensional lattice with multiple atoms per basis, we do not necessarily have a closed form expression for $\omega(K)$, so we consider two approximations to get around this shortcoming.

**Debye model for density of states**

In the Debye model, the velocity of sound (i.e. the wave propagation velocity) is taken as a constant (v) for every polarization, as it was in our derivation of elastic waves in a continuous solid (Ch 3). Clearly, this model is meant to only approximate acoustic phonons, not optical ones.

$$\omega \equiv vK$$

The density of states becomes (using expression above, and substituting $K = \omega/v$):

$$D(\omega) = \frac{\left(\frac{\omega}{v}\right)^2 V}{2\pi^2} \frac{d}{d\omega}\left(\frac{\omega}{v}\right)$$

$$D(\omega) = \frac{\omega^2 V}{2\pi^2 v^3}$$

If there are N primitive cells in the solid, there are N acoustic phonon modes.

With this information, a 'cutoff' frequency can be determined:

$$N = \frac{K^3 V}{6\pi^2} = \frac{\omega^3 V}{6\pi^2 v^3}$$

Define the 'cutoff frequency' as $\omega_D$ (D is for debye) and plug in above.

$$\omega_D^3 = \frac{6\pi^2 v^3 N}{V}$$

Because $\omega$ is a function of K, this also defines a cutoff wavevector $K_D$:

$$K_D = \frac{\omega_D}{v} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

The internal energy as a function of temperature is given by (counting only one polarization type; we are only considering acoustic branches so there will be **three** polarization types):

$$U = \int d\omega D(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} = \int_0^{\omega_D} d\omega \left(\frac{\omega^2 V}{2\pi^2 v^3}\right) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

(assume speed of sound is the same for all polarization types and multiply by 3)

$$U = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

Make substitution: $x \equiv \frac{\hbar\omega}{k_B T}$

$$\omega = xk_BT/\hbar$$

$$d\omega = \frac{k_BT}{\hbar}dx$$

$$x_D \equiv \hbar\omega_D/k_BT \equiv \theta/T$$

$\theta$ is defined as the debye temperature (the temperature equivalent of the debye temperature). It is given by:

$$\theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

$$\theta^3 = \left(\frac{\hbar v}{k_B}\right)^3 \frac{6\pi^2 N}{V}$$

$$\left(\frac{T}{\theta}\right)^3 = \frac{T^3 k_B^3 V}{6\pi^2\hbar^3 v^3 N}$$

Plug all this into expression for U:

$$U = \frac{3V\hbar}{2\pi^2 v^3}\left(\frac{k_BT}{\hbar}\right)^3 \frac{k_BT}{\hbar}\int_0^{x_D} dx\frac{x^3}{e^x - 1}$$

$$U = 9Nk_BT\left(\frac{T}{\theta}\right)^3\int_0^{x_D} dx\frac{x^3}{e^x - 1}$$

The heat capacity is found by differentiating with respect to temperature. It is easier to do this back when U was in terms of $\omega$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}(\frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\frac{\omega^3}{e^{\hbar\omega/k_BT} - 1})$$

$$C_V = \frac{3V\hbar}{2\pi^2 v^3}\frac{\hbar}{k_BT^2}\int_0^{\omega_D} d\omega\frac{\omega^4 e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT} - 1)^2}$$

Re-express in terms of x

$$C_V = 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{x_D} dx\frac{x^4 e^x}{(e^x - 1)^2}$$

The integral can be solved numerically, and approximations can be made in limits of low and high temperature.

**Low temperature limit:**

In the low temperature limit, we let the upper bound of the integral go to infinity. We will solve the integral for the energy U and differentiate afterwards.

$$\int_0^\infty dx\frac{x^3}{e^x - 1} = \int_0^\infty dx\, x^3\sum\nolimits_{s=1}^{\infty} e^{-sx} = 6\sum_{s=1}^{\infty} 1/s^4 = \pi^4/15$$

The second to last step comes from multiple applications of integration-by-parts and the last step is from a standard table.

Thus, in the limit of very low temperature, $U \approx 3\pi^4 Nk_B T^4/5\theta^3$

And $C_V \approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta}\right)^3$

Thus, in the limit of low temperature, the lattice specific heat is proportional to $T^3$, which is verified by experiments.

**High temperature limit:**

In the high temperature limit $x \to 0$ and we can taylor expand all of the exponential terms to first order

$$C_V = 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4(1+x)}{(x)^2} = 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx(x^2 + x^3)$$

$$C_V = 9Nk_B \left(\frac{T}{\theta}\right)^3 \left(\frac{1}{3}x_D^3 + \frac{1}{4}x_D^4\right)$$

Drop higher order terms and consider definition of $x_D$ given earlier in terms of $\theta$

$$C_V \approx 3Nk_B \left(\frac{T}{\theta}\right)^3 \left(\frac{\theta}{T}\right)^3 = 3Nk_B$$

This is the **classical** value of the heat capacity, in which each atom contributes $3k_BT$ to the total energy, and there are N atoms, so the temperature derivative of the total energy is $3Nk_B$. Heat capacity for a general crystalline solid and for specific crystalline solids are plotted below.

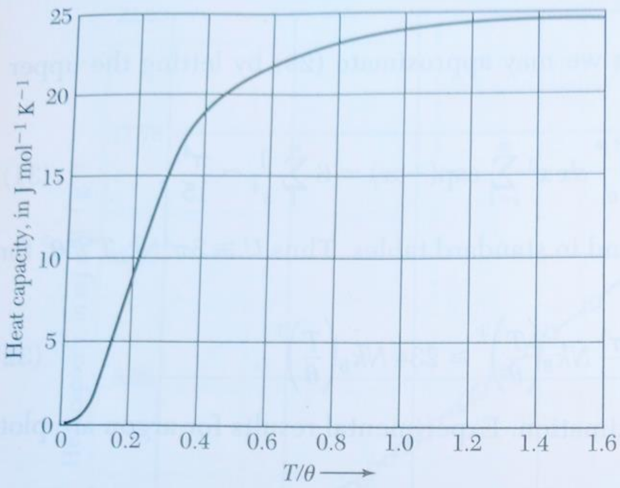


**Figure 7** Heat capacity $C_V$ of a solid, according to the Debye approximation. The vertical scale is in J mol$^{-1}$ K$^{-1}$. The horizontal scale is the temperature normalized to the Debye temperature $\theta$. The region of the $T^3$ law is below $0.1\theta$. The asymptotic value at high values of $T/\theta$ is 24.943 J mol$^{-1}$ deg$^{-1}$.

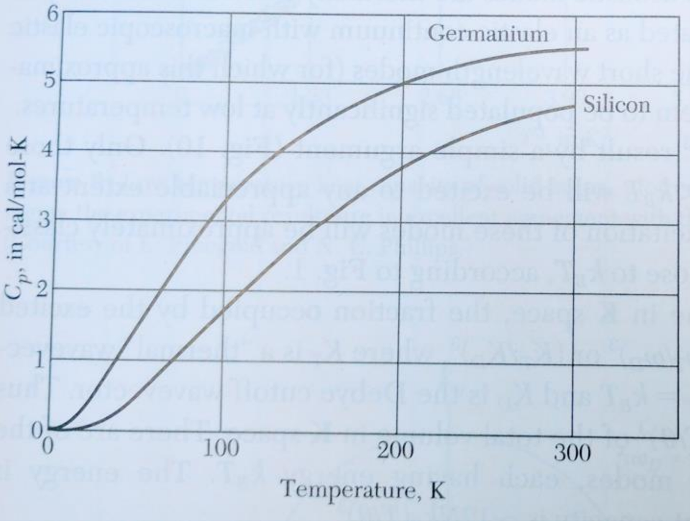


**Figure 8** Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K, multiply by 4.186.

Notice that the classical value of the heat capacity is reached pretty much at the debye temperature ($\theta$). Thus, the debye temperature physically represents the temperature when phonons in a solid start behaving like a classical gas of particles. Some debye temperatures for real materials are given below:

| | | | |
|---|---|---|---|
| Aluminium | 428 K | Manganese | 410 K |
| Beryllium | 1440 K | Nickel | 450 K |
| Cadmium | 209 K | Platinum | 240 K |

| | | | |
|---|---|---|---|
| Caesium | 38 K | Sapphire | 1047 K |
| Carbon | 2230 K | Silicon | 645 K |
| Chromium | 630 K | Silver | 215 K |
| Copper | 343.5 K | Tantalum | 240 K |
| Gold | 170 K | Tin (white) | 200 K |
| Iron | 470 K | Titanium | 420 K |
| Lead | 105 K | Tungsten | 400 K |

Notice that

- Many are close to room temperature
- ‘Soft’ metals such as gold and lead have a low debye temperature
- Materials containing ‘light’ elements such as carbon, beryllium, and sapphire (Al2O3) have very high debye temperature